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Synthesis of $W_{18}O_{49}$ Phase by Carbothermal Reduction of Tungsten Oxide and its Field Emission Characteristics

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Abstract We report a carbothermal reduction process for massive synthesis of monolithic $W_{18}O_{49}$ phase from tungsten oxide in the presence of carbon source. Carbon black powder was used as a carbon source and added to WO_3 by 40 weight percent. Bundles of $W_{18}O_{49}$ rods were formed over the temperature range of 800°C to 900°C. Pure $W_{18}O_{49}$ bundles could be separated from the mixture of $W_{18}O_{49}$ and residual carbon black powder. Field emission character of $W_{18}O_{49}$ phase was determined using the extracted $W_{18}O_{49}$ rods. Flat lamp fabricated from the $W_{18}O_{49}$ rods showed the turn-on field of 9.3 V/μm.

Keywords : Massive synthesis of $W_{18}O_{49}$, Carbothermal reduction, Field emission characteristics

1. Introduction

Tungsten oxide is an attractive material for electrochromic applications, sensors, and a source material for tungsten metal (W) powder[1-3]. There are several types of tungsten oxide such as WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$, and WO_2. Recently the tungsten oxides such as $W_{20}O_{58}$, $W_{18}O_{49}$, and WO_2, so called tungsten sub-oxide, attract much attention because of their peculiar properties such as superconducting property and high charge mobility[4].

$W_{18}O_{49}$ oxide with a monoclinic crystal structure is usually obtained in the form of rods through oxidation of tungsten wire or tungsten foil[5-6]. Recently the $W_{18}O_{49}$ material was reported to have a possibility as a source of field emission for display devices[7] but has limitations in reproducibility and mass production.

The tungsten oxide is reduced to metallic state through a complex kinetic route comprising of several tungsten sub-oxides. A reduction route generally accepted is $WO_3 \rightarrow W_{18}O_{49} \rightarrow WO_2 \rightarrow W$[8-9]. Among the various reduction processes, a carbothermal reduction method has been generally adapted to make W powder because of its simplicity and cost effectiveness. During the carbothermal reduction, the tungsten oxide powder admixed with carbon powder (carbon black powder or graphite powder) is heated up to about 1000°C under hydrogen atmosphere[10]. Most of studies in the carbothermal reduction of tungsten oxide have been focused on the production of tungsten and tungsten carbide powder[8-13]. Until now there are no systematic studies on the kinetics of carbothermal reduction to obtain a specific tungsten sub-oxide, for example, a $W_{18}O_{49}$ phase.

In the present study, we developed a high-yield synthesis process of $W_{18}O_{49}$ phase material by a carbothermal reduction of tungsten oxide and subsequently fabricated a simple device for the measurement of field emission behavior of $W_{18}O_{49}$ rods.

2. Experimental Method

Tungsten oxide powder (WO_3) of commercial product was purchased and admixed with carbon black powder as the carbon source. A powder mixture of WO_3 and 40% carbon black was put into a stainless steel jar with tungsten carbide balls and milled in a slurry state with ethanol as a milling media for complete mixing and particle refinement.

The milled slurry was dried in a vacuum oven. The milled powder mixture was put into a graphite boat, heated to the desired temperature in the range of 700°C to 900°C and kept for predetermined time from 0.5 h to 8 h, respectively, for carbothermal reduction

in a tube furnace under flowing nitrogen gas. The morphology and phase(s) of the treated powder were determined by a scanning electron microscope (FE-SEM, Philips XL-30) and X-ray diffraction method (XRD, Philips PW-1830).

In order to observe a field emission behavior of $W_{18}O_{49}$, the $W_{18}O_{49}$ rods were separated from the heat-treated powders with a gravimetric settling method and fabricated into a flat lamp with two square electrodes of one inch diagonal. The separated pure $W_{18}O_{49}$ rods were mixed homogeneously with terpinol (Junsei) and ethyl-cellulose (Aldrich) at 50°C. A $W_{18}O_{49}$ paste was printed using a silk screen of 325 mesh on the surface of ITO film electrode (cathode) sputtered on a soda-lime glass plate. Anode electrode was fabricated along with the same method with cathode fabrication and then a phosphor powder was coated on the surface of anode. Field emission behaviors of J (emission current density)-V (voltage) and fluorescence were determined with a gap of 300μm between anode and cathode electrodes.

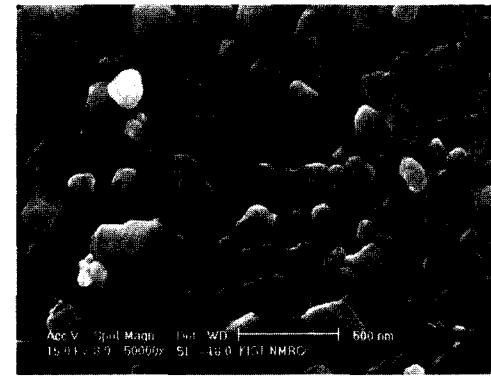
3. Results and Discussion

3.1. Synthesis of $W_{18}O_{49}$ phase

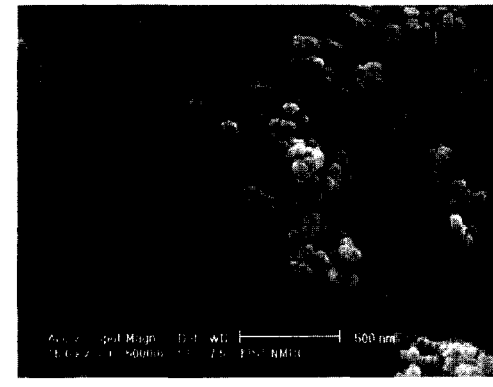
Figure 1 shows the SEM micrographs of WO_3 powder (a), carbon black powder (b), and milled mixture of WO_3 and 40% carbon black (c). All the powders are very fine and the milled mixture was very homogeneous.

Figure 2 shows the SEM micrographs of powder mixtures treated at the various temperatures for 2 h. The milled powder showed almost no morphology change below 800°C. Rod-shaped crystals appeared in the fine particle matrix above 850°C and grew further at 900°C.

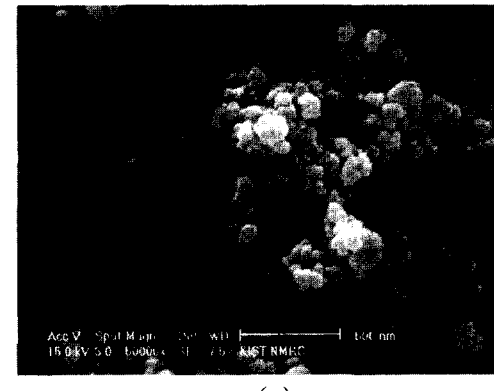
Figure 3 shows the X-ray diffraction patterns of the same samples shown in Figure 2. The WO_3 phase remained intact at least up to 800°C. The whole WO_3 phase transformed to a $W_{18}O_{49}$ phase at 850. A part of $W_{18}O_{49}$ phase was dissociated into WO_2 at 900°C. Comparing Figures 2 and 3 with each other, the rod-type crystals formed in the powder mixture were identified as a $W_{18}O_{49}$ phase, but $WO_{2.9}$ and WO_2 phases appearing in the X-ray diffraction patterns could not be distinguished from the residual carbon black particles by morphology although they were considered to have a spherical shape. It is evident from Figure 3 that pure $W_{18}O_{49}$ phase can be synthesized without other types of tungsten sub-oxide from the mixture of WO_3-carbon black powder.



(a)



(b)



(c)

Fig. 1. The SEM micrographs of raw powders: (a) WO_3, (b) carbon black, and (c) milled powder mixture.

Figure 4 is a series of SEM micrographs obtained by varying the treatment temperature and time, respectively. At 700°C small fraction of $W_{18}O_{49}$ phase

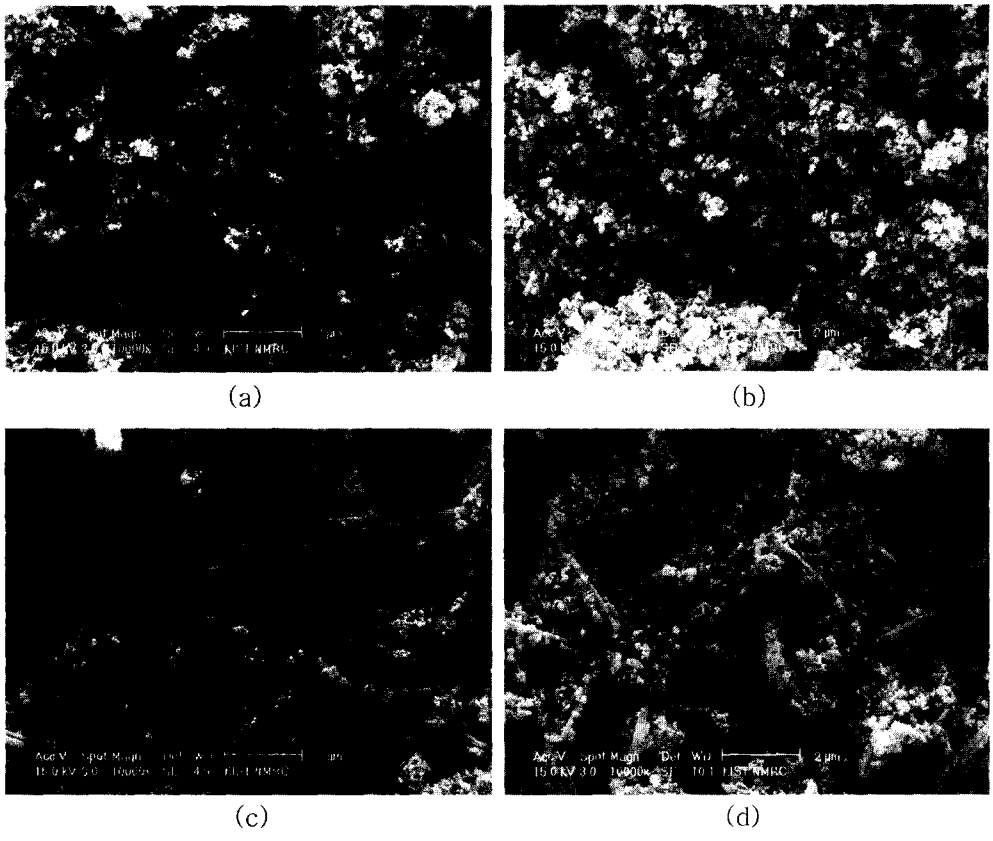


Fig. 2. The SEM micrographs of powder mixtures heat-treated for 2 h at the various temperature: (a) 700°C, (b) 800°C, (c) 850°C, and (d) 900°C.

formed slowly after 8 h. At 900°C the $W_{18}O_{49}$ phase was already under dissociation into WO_2 phase even after 0.5 h, which meant that the $W_{18}O_{49}$ phase had formed either within 0.5 h at 900°C or during heating up to 900°C. It is evident that an optimum condition for high yield synthesis of $W_{18}O_{49}$ phase is at around 850°C for longer than 4 h. However, when the powder mixture was treated longer than 4 h, very thick bundles of $W_{18}O_{49}$ were obtained. The $W_{18}O_{49}$ rods in the bundles look very tightly bonded to each other. Less agglomerated $W_{18}O_{49}$ rods are required to determine their field emission property. Therefore we chose the condition of 850°C and 2 h in order to obtain individually separated $W_{18}O_{49}$ rods as many as possible.

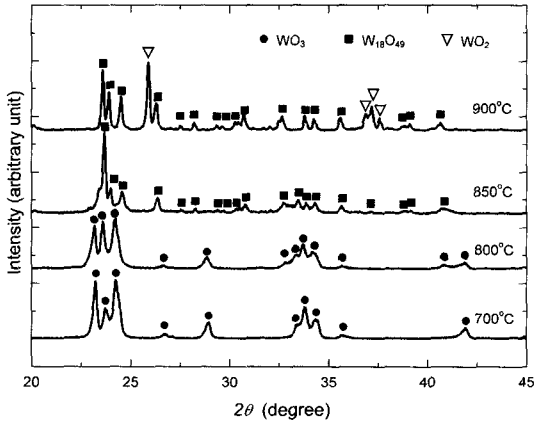


Fig. 3. The X-ray diffraction patterns of the samples shown in Fig. 2.

3.2. Field emission behavior of $W_{18}O_{49}$ phase

Figure 5 shows the morphology of $W_{18}O_{49}$ rods separated from the powder mixture treated at 850°C for 2 h. Even though the $W_{18}O_{49}$ phase in the treated specimen looked individually separated as shown in Figure 4 (850°C, 2 h), the separated $W_{18}O_{49}$ rods were in the

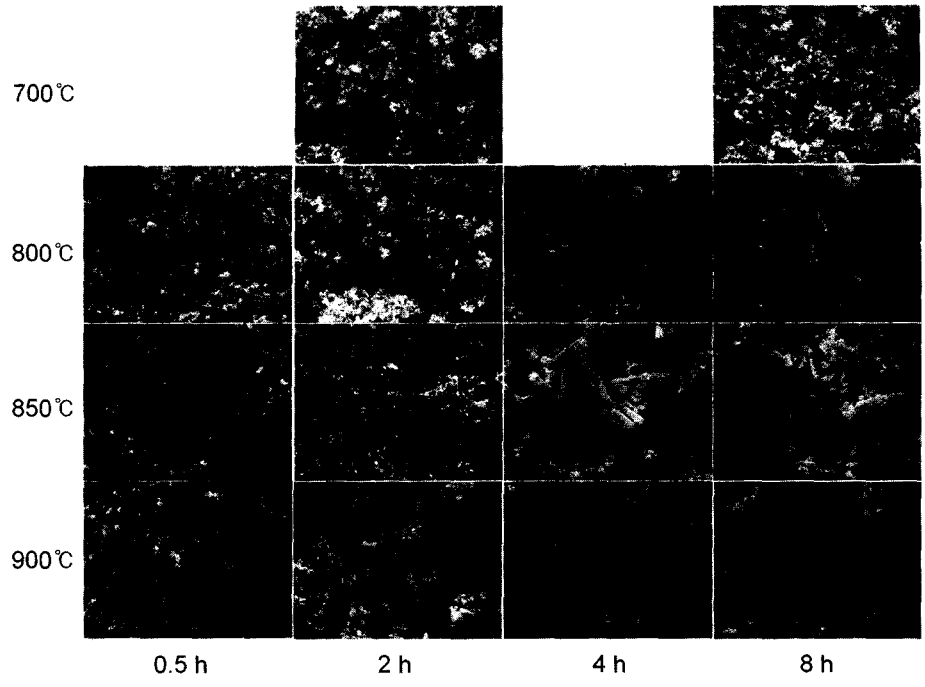


Fig. 4. A series of SEM micrographs of the powder mixture treated over the temperature between 700°C and 900°C for predetermined time from 0.5 h to 8 h.

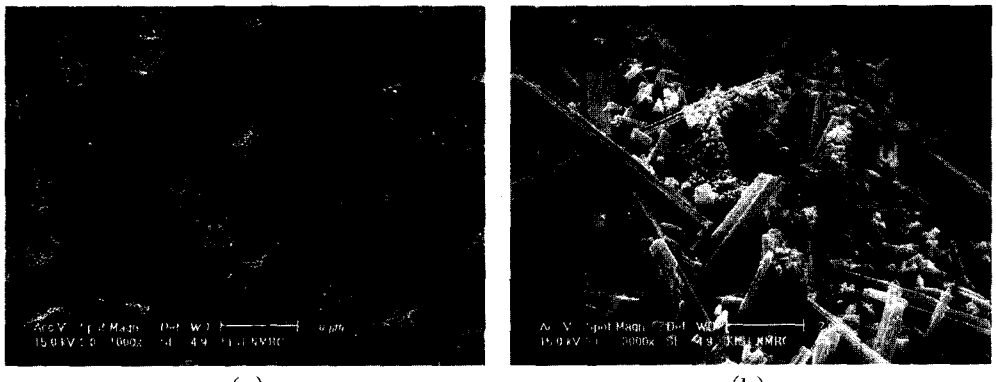


Fig. 5. The SEM micrographs of pure $W_{18}O_{49}$ rods separated from the mixture treated at 850°C for 2 h: (a) low magnification and (b) high magnification.

bundles. The long bundles in the mixture seemed to have been chopped into the short bundles during separation.

Figure 6 shows the light emitting patterns observed from the flat lamp with 300 μm gap between electrodes as the applied voltage increased. The lamp turned on at 2,000 V and the light became brighter and brighter as the applied voltage increased. A relationship between applied voltage and current density in the flat lamp was shown in Figure 7. Referring to the definition of turn-on field as the electric field required to produce a current of 10 μA/cm^2 [7], the flat lamp fabricated in the present study had a turn-on field of 9.3 V/μm. Comparing with turn-on field of 2.6 V/μm in Reference 7, quite high value of turn-on field in the present study is attributed to either a bundle shape of $W_{18}O_{49}$ rods or irregularity in the bundle size

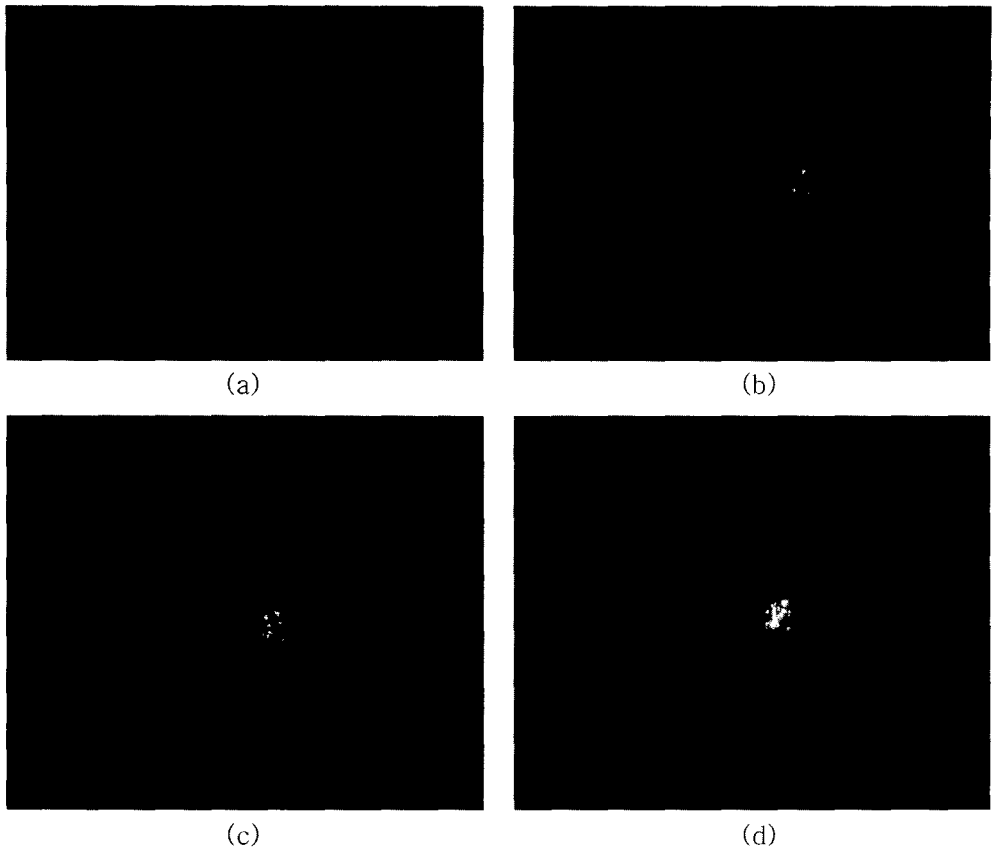


Fig. 6. Light emitting patterns of the flat lamp fabricated from the $W_{18}O_{49}$ rods with applied voltage : (a) 2,000V, (b) 2,200V, (c) 2,600V, (d) 2,800V. (The distance between electrodes was fixed by 300 μm.)

with the effect of align. Further study is necessary to improve field emission properties of $W_{18}O_{49}$ rods, for example, a new optimization for synthesis of individually separated rods.

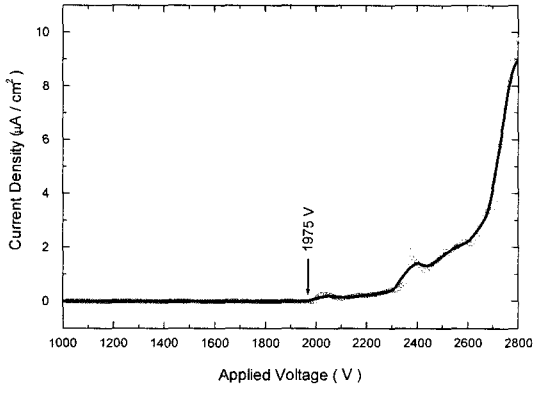


Fig. 7. Variation of field emission current with applied voltage obtained from the $W_{18}O_{49}$ bundle emitters.

4. Conclusions

Large quantity of monolithic $W_{18}O_{49}$ phase was successfully synthesized from the mixture of WO_3 and carbon black powders. The bundles of $W_{18}O_{49}$ rods were formed over the temperature region from 700°C to 900°C. The optimum condition for massive synthesis of monolithic $W_{18}O_{49}$ phase was proved as 850°C and 4 h under flowing nitrogen gas. The pure $W_{18}O_{49}$ rods could be easily separated from the treated samples by the gravimetric settling method. The flat lamp fabricated using the bundles of $W_{18}O_{49}$ rods exhibited a characteristic emission behavior of the turn-on field of 9.3 V/μm, which was quite higher value than that reported. The morphology of $W_{18}O_{49}$ phase needs to

be controlled to the individually separated rods for property measurement including the field emission property in the future.

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